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CATALYTIC ANODES IN CHROMIUM DEPOSITION

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Catalytic anodes based on IrO_2 catalyst has been investigated as a substitute for lead in chromium deposition from chromic acid electrolyte. Oxygen evolution characteristics and ability to oxidise the trivalent chromium are some of the aspects examined in this context. Comparison has also been made with conventional lead anodes.

Key words: Chromium deposition, catalytic anodes, chromium acid, electro-deposition

INTRODUCTION

Lead anodes, insoluble in chromic acid, are customarily used in electroplating and electrowinning of chromium from the chromic acid electrolyte. Pb-Sb, Pb-Sn, Pb-Ag are some lead alloys commonly used. Oxygen evolution is the anodic reaction and it is always associated with higher overpotential resulting in higher cell voltage. The increased permeability of the anodic passive layers and their susceptibility to mechanical stress formation are the main reasons for the enhanced corrosion of the lead anodes in chromic acid electrolyte. Moreover, lead anodes tend to become passive during idle periods and require electrolysis with higher voltage for reactivation.

One of the side reactions in the chromium deposition operation is the formation of Cr^{3+} ions which gradually build up in the electrolyte and an excess Cr^{3+} must be removed or converted into Cr^{6+} to keep the Cr^{3+} concentration at a suitable level. The layer of PbO_2 formed on the anodes during use causes the trivalent chromium to be reoxidised continuously to chromic acid, thereby keeping its concentration at a low level.

The introduction of dimensionally stable anodes (DSA) in chlor-alkali industries with significant energy savings led to attempts on the use of such anodes in other industrial electrolytic processes. A straight forward reduction in oxygen overpotential is the primary advantage sought in such anode systems for the processes where oxygen evolution is the anodic reaction. Reduced maintenance problems and less anode corrosion are the other advantages. Materials like RuO_2 and IrO_2 show good characteristics as catalysts for oxygen evolution [1].

Use of catalytic anodes based on IrO_2 catalyst for chromium deposition in chromic acid electrolyte has been investigated in the work now being reported. Oxygen evolution characteristics and the ability to oxidise the trivalent chromium are some of the aspects examined in this context. A comparison has also been made with the conventional lead anode.

EXPERIMENTAL

Sponge-type catalytic anodes were prepared by activating the titanium sponge particles with $IrCl_3$ solution at 673K and embedding these particles onto lead substrate. Similarly sheet-type anodes were prepared by forming an active coating of IrO_2 onto titanium strips. Potentiodynamic studies were carried out using a potentioscan coupled with an x-y recorder in the oxygen evolution potential region. Galvanostatic studies were carried out using a galvanostat of 1A capacity. 1M chromic acid was used as the electrolyte and sheet type catalytic anodes and lead anodes of 1 cm^2 area were used. An H-type cell was employed and a platinum foil was used as auxiliary electrode. Potentials were measured against a saturated calomel electrode (SCE).

Electrodeposition of chromium was carried out on long term basis using sponge-type catalytic anodes in an electrolyte containing 250 $g.l^{-1}$ chromic acid and 2.5 $g.l^{-1}$ H_2SO_4 at a cathodic current density of 300 $mA.cm^{-2}$ and Cr^{3+} developed in the electrolyte was analysed periodically. A colorimetric procedure was followed for the estimation of Cr^{3+}, where the optical density was recorded at a wave length of 570 nm.

0.1M sulphuric acid solutions containing 5-50 $g.l^{-1}$ Cr^{3+} were electrolysed at an anode current density of 50 $mA.cm^{-2}$ in a diaphragm cell using sponge-type catalytic anodes and current efficiency for oxidation of Cr^{3+} was found out and comparison was made with Pb anode.

RESULTS AND DISCUSSION

Fig.1 shows the potentiodynamic curves of lead and sheet type catalytic anodes of IrO_2 catalyst in 1M chromic acid solution in the potential region of oxygen evolution. Oxygen evolution starts at 1.25V for the catalytic anode and at 1.45V for the lead anode. An anode potential saving of 200-250 mV is maintained even at higher current densities, as seen from the potentiodynamic curves. Similar observation has been reported for sulphuric acid solutions also [2]. Fig.2 shows the Tafel plots for oxygen evolution on lead and catalytic anodes. A Tafel slope of 60 mV is obtained for the catalytic anode while 120mV is obtained for Pb, indicating the catalytic effect of IrO_2 on oxygen evolution. This data agrees with the reported value of 50-56 mV for IrO_2 in acid solutions [1]. Generally electrocatalytic activity is characterized in terms of overpotential, (η) at constant apparent current density, (I). Exchange current density, (I_o) is often used to classify the electrocatalysts but this can be correct only if the observed Tafel slopes have the same value. But the rate of change of I with η, viz. the slope of the graphical relationship between E and log I is more useful for

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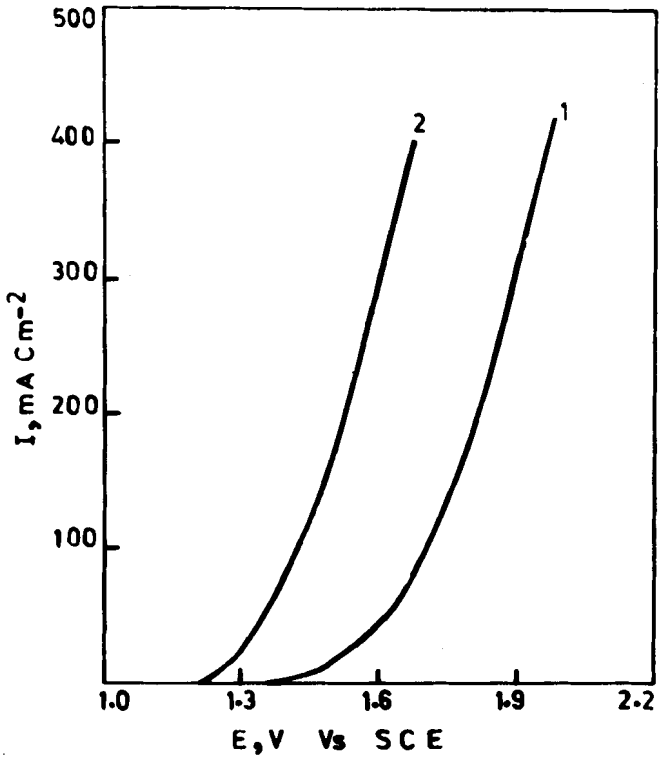

Fig.1: Potentiodynamic curves for O_2 evolution in 1M H_2CrO_4 at 10mV s^{-1}; (1) Lead, (2) Catalytic anode

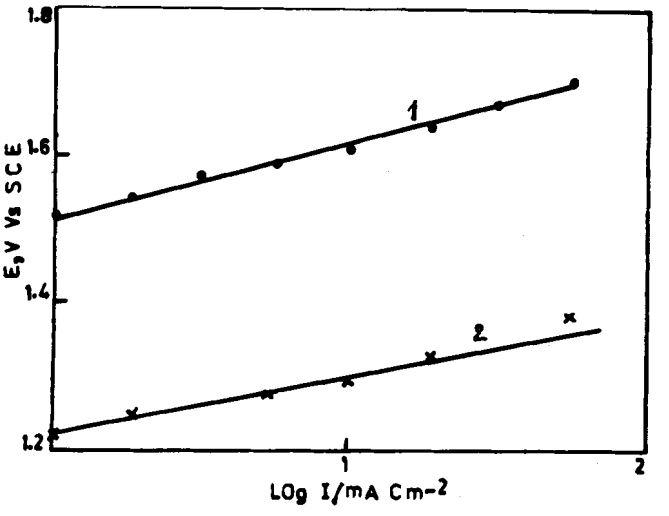

Fig.2: Polarisation curves for O_2 evolution in 1M H_2CrO_4 (1) Lead, (2) Catalytic anode

evaluating electrocatalysis from the view point of practical use. Hence electrodes with lower Tafel slope can be good electrocatalysts at higher overpotentials.

Table I shows the build up of Cr^{3+} in the chromic acid electrolyte during electrodeposition of chromium on long term basis. In the case of lead, where the ratio of the anode to cathode current density is 1:1, the Cr^{3+} concentration stabilizes at 5.25 $g.l^{-1}$.

TABLE I: Build up of Cr^{3+} in the electrolyte:Electrolyte = 250 $g.l^{-1}$ chromic acid and 2.5 $g.l^{-1}$ H_2SO_4;Cathodic current density 300 $mA.cm^{-2}$

Anode	Anode c.d. ($mA.cm^{-2}$)	Cr^{3+} content at different intervals ($g.l^{-1}$)			
		24 hr	48 hr	72 hr	168 hr
Lead	300	2.00	3.25	5.25	5.25
	75	5.25	2.25	2.25	2.25
Catalytic anode	300	2.25	4.0	4.75	4.75
	150	2.60	4.0	6.00	7.90
	75	5.75	8.0	10.00	16.00

When the anode area is increased by 4 times, Cr^{3+} is maintained at 2.25 $g.l^{-1}$. The higher surface area of the anode facilitates oxidation of Cr^{3+} developed in the electrolyte during chromium deposition. It is evident that the anodic reaction in chromium deposition consists of oxygen evolution and oxidation of chromic ions:

$$2\,H_2O = O_2 + 4H^+ + 4e \qquad E_0 = 1.23V\ (NHE) \qquad \ldots (1)$$

and

$$2\,Cr^{3+} + 7\,H_2O = Cr_2O_7^{2-} + 14H^+ + 6e \qquad E_0 = 1.33V\ (NHE) \ldots (2)$$

From the thermodynamic point of view both processes can occur in the range of current density studied. In fact, reaction (2) takes place efficiently on the lead anode as the overpotential on Pb is higher. In the case of Pb anodes, the tendency for build up of Cr^{3+} is less at increased anode area, indicating the effective oxidation of Cr^{3+} to Cr^{6+} at lower anode current densities. Generally an increase in current density favours oxygen evolution to the detriment of the other oxidations. This kind of situation frequently arises where oxygen evolution proceeds concurrently with another Faradaic reaction.

When catalytic anodes are used in the place of Pb, the rate of build up of Cr^{3+} is relatively higher, indicating the ineffective oxidation of Cr^{3+} on the catalytic surface. Oxygen evolution is facilitated on the catalytic anodes and under these conditions the side reaction, viz. the oxidation of Cr^{3+} takes place to a lesser extent. A progressive increase in Cr^{3+} content is observed with time of electrolysis and in a period of one week, it reaches 16 $g.l^{-1}$ as against a stabilized value of 2.25 $g.l^{-1}$ with lead anodes. Similar behaviour has been reported for the platinized titanium with the active coating of IrO^2 [3]. In chromic acid electrolysis and the addition of surface active species like fluosilicate shifts the anode potential to the more positive value facilitating the oxidation of Cr^{3+} ions. Another significant observatin made in the present

study is that the build up of Cr^{3+} is prominent when the active surface area is higher in contrast to the situation existing with Pb anodes. This may be due to the fact that when the catalytic surface area is increased, the anodic depolarization is still higher and oxygen evolution is further facilitated. Correspondingly the other anodic reaction of Cr^{3+} oxidation, which requires a little higher overpotential, proceeds to lesser extent.

Cell voltage measurements made during long term electrolysis indicate a steady value of 2.9V for Pb. For the catalytic anodes it is 2.45V initially at an anode current density of 75 $mA.cm^{-2}$ and 2.77V at the end of one week. The cell voltage is found to rise gradually as the Cr^{3+} content in the electrolyte builds up in the course of the deposition. As the conductivity of Cr^{3+} is lower than that of Cr^{6+}, the rise in cell voltage is due to increase in the resistance of the electrolyte.

Further evidence for the inhibition of Cr^{3+} oxidation on catalytic anodes has been obtained in the experiments where the sulphuric acid solutions of trivalent chromium is electrolysed in a diaphragm cell using catalytic anodes. The current efficiency for the conversion of Cr^{3+} to Cr^{6+}, as seen from the Table II is only 1% with catalytic anodes whereas it is nearly 50% with the conventional lead anodes.

TABLE II : Current efficiency for oxidation of Cr^{3+} on lead and catalytic anodes for different concentrations of Cr^{3+}
Current density = 50$mA.cm^{-2}$; 0.1M H_2SO_4

Cr^{3+} concentration ($g.l^{-2}$)	Current efficiency (%)	
	Lead	Catalytic anode
5	51.2	1.0
10	53.7	1.0
50	55.8	1.0

CONCLUSION

Anodic polarisation studies indicate an anode potential reduction of nearly 250 mV in the electrodeposition of chromium with the catalytic anodes of IrO_2 electrocatalyst. The continuous usage of these anodes results in the build up of considerable amount of trivalent chromium in the chromic acid electrolyte. The active sites promote oxygen evolution and under these conditions of anodic depolarization, the side reaction at the anode, viz. $Cr^{3+} \rightarrow Cr^{6+}$ becomes less predominant. The gradual build up of Cr^{3+} in the electrolyte results in the slow rise of cell voltage and advantage of potential saving realised initially is thus lost in the course of the deposition operation.

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